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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C09K 7/02, 7/06	A1	(11) International Publication Number: WO 94/28085 (43) International Publication Date: 8 December 1994 (08.12.94)						
<p>(21) International Application Number: PCT/NO94/00097</p> <p>(22) International Filing Date: 25 May 1994 (25.05.94)</p> <p>(30) Priority Data:</p> <table border="0"><tr><td>931954</td><td>28 May 1993 (28.05.93)</td><td>NO</td></tr><tr><td>933288</td><td>15 September 1993 (15.09.93)</td><td>NO</td></tr></table> <p>(71) Applicant (for all designated States except US): DEN NORSKE STATS OLJESELSKAP A.S. [NO/NO]; Forus, Postboks 300, N-4001 Stavanger (NO).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): SUNDE, Egil [NO/NO]; Draugveien 30, N-4300 Sandnes (NO). JOHNSEN, Hans, Konrad [NO/NO]; Nøtteberget 17, N-7500 Stjørdal (NO).</p> <p>(74) Agent: TANDBERGS PATENTKONTOR AS; Boks 7085, N- 0306 Oslo (NO).</p>		931954	28 May 1993 (28.05.93)	NO	933288	15 September 1993 (15.09.93)	NO	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. In English translation (filed in Norwegian).</p>
931954	28 May 1993 (28.05.93)	NO						
933288	15 September 1993 (15.09.93)	NO						
<p>(54) Title: PLUGGING LIQUID FOR PLUGGING A SUBTERRANEAN FORMATION ZONE</p> <p>(57) Abstract</p> <p>A plugging liquid for plugging of a zone of a subterranean formation around a drill hole, consisting of an emulsion comprising (a) a continuous phase containing a hydrophobic liquid, an emulsifier and a crosslinking agent for a polysaccharide, and (b) a discontinuous phase containing water and a polysaccharide. A variant of the plugging composition contains in addition a weighting material in the discontinuous phase. Also described is a method for preparing the plugging liquid and a method for plugging a zone of a subterranean formation penetrated by a drill hole in fluid communication with the zone, according to which method the new plugging liquid is injected into the zone via the drill hole and is subjected to high shear forces in the drill hole, whereby the polysaccharide and the crosslinking agent are brought into contact with one another with resulting initiation of a crosslinking of the polysaccharide and a setting of the plugging liquid. When the drilling liquid contains a weighting material it is primarily used to inhibit or prevent an undesired blow-out in or from a well.</p>								

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PLUGGING LIQUID FOR PLUGGING A
SUBTERRANEAN FORMATION ZONE.

5 This invention relates to a plugging liquid on emulsion basis,
a method for its preparation and a method for plugging a zone
of a subterranean formation penetrated by a drill hole.

A large number of gel forming compositions are known in the
10 art for use as well control liquids in the drilling of wells
for the recovery of oil and gas, for instance in cases where
well liquids are lost to the formation or liquid or gas is
flowing into the well from the formation. It is known to use
polysaccharides for thickening purposes in such known gel
15 forming compositions, see e.g. Norwegian Patents Nos. 116,667
and 161,635, US Patent No. 4,634,538 and British Patent No.
1,406,513.

It is also known to utilize as plugging liquids so-called
20 "rheotropic" liquids. These liquids thicken when subjected to
high shear stress. The rheotropic liquid must have physical
characteristics enabling it to be easily pumped through the
mud system (Condition 1) to the drill bit when leakages occur
in the formation. The shear stress created when the liquid is
25 forced through the nozzles of the drill bit, where the press-
ure drop will be in the range of about 50 to 120 bars, must
result in a thickening of the liquid (Condition 2). The time
before thickening must however be sufficient for the liquid to
flow into and seal the formation.

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US Pat. No. 4,663,366 (Carr Corporation) discloses a rheo-
tropic liquid of such a nature and an emulsion technique for
controlling the thickening of the liquid. According to said
patent, a polycarboxylic acid-containing water-in-oil emulsion
35 is used wherein:

- the oil phase contains dispersed therein a hydratable,
water-swelling, hydrophilic clay such as bentonite, and addi-
tionally contains a solubilized surfactant consisting of a
polyamine derivative, and

- the aqueous phase contains dissolved therein a polyacrylamide and a polycarboxylic acid.

It is critical that the bentonite be kept separated from the water until the required thickening of the liquid is initiated. For that purpose each droplet of the dispersed aqueous phase is coated with a membrane or a film of a polymeric material which is formed as a consequence of the aqueous phase being dispersed or emulsified in the oil phase of the emulsion. The film or membrane is formed as a result of the interfacial interaction between the polyamine derivative in the oil phase and the polyacrylamide and the polycarboxylic acid in the dispersed aqueous phase. When the emulsion is subjected to high shear forces, the protective film around the dispersed droplets in the emulsion is broken and the bentonite comes into contact with the water, thus enabling a swelling of the bentonite and consequently a thickening of the liquid. However, for the rheotropic liquid of US Pat. No. 4,663,366 the obtainable ratio of the thickness of the liquid in Condition 2 to the thickness of the liquid in Condition 1 is lower than is desirable.

There is a need in well control operations for improved plugging liquids which (1) have the lowest possible viscosity in Condition 1, before they are subjected to high shear forces, (2) thickens to a high thickness in Condition 2 after having been subjected to high shear forces, (3) maintain their acquired thickness for a longer period of time, and (4) to the least possible extent undergo a thickening in Condition 1 as a result of the emulsion gradually deteriorating during storage or before it has had time to pass through the nozzles of the drill bit in the drill hole.

It is an object of the present invention to provide a plugging liquid exhibiting markedly improved properties compared to the plugging liquids that are available today.

Thus, the invention provides a new plugging liquid for plugging a zone of a subterranean formation around a drill hole,

consisting of an aqueous liquid containing a polysaccharide. The plugging liquid is characterized in that it consists of an emulsion comprising:

- a) 5 - 50% by volume of a continuous phase containing:
- | | | |
|---|-------------|---|
| 5 | 800 - 998.5 | ml/l of a hydrophobic liquid, |
| | 0.5 - 100 | ml/l of an emulsifier, and |
| | 1 - 100 | g/l of a crosslinking agent for a polysaccharide, |
- b) 50 - 95% by volume of a discontinuous phase containing:
- | | | |
|----|-----------|--------------------------|
| 10 | 950 - 997 | ml/l of water, and |
| | 3 - 50 | g/l of a polysaccharide. |

Like the emulsion of US Pat. No. 4,663,366 discussed above, the new emulsion makes use of an emulsion technique involving storing of reactants separately, one in each phase of the emulsion. When the reactants utilized in the new emulsion, viz. the polysaccharide and the crosslinking agent, come into contact with one another after the emulsion having been subjected to high shear forces, a crosslinking of the polysaccharide is taking place, resulting in a setting of the emulsion to a gelatinous solid substance.

The principle of the setting of the new plugging liquid is different from that of the plugging liquid of US Pat. No. 4,663,366. It is the crosslinking of the polysaccharide that causes the setting of the emulsion, whereas in the emulsion of US Pat. No. 4,663,366 a thickening takes place as a result of a swelling of the bentonite when the latter comes into contact with water. The setting achieved with the new plugging liquid of the invention is a substantially irreversible setting and has a good durability within the periods of time that are of interest in normal rig operations.

The mud system employed in well and formation treatment operations consists of a number of units, each of which exerts shear stress to a greater or lesser extent on the flowing liquid. The shear stress is closely related to the pressure drop in each individual unit. The highest pressure drop and thus the highest shear stress occurs e.g. during the passage

of the nozzles in a drill bit or a port in a completion string down in a well. The use of the plugging liquid of the invention is based on the condition that only the nozzles of the drill bit or similar restrictions should produce a sufficiently high shear stress for the reactants (polysaccharide and crosslinking agent) to come into contact with one another, with a resulting crosslinking of the polysaccharide and setting of the liquid.

- 10 The hydrophobic liquid of the plugging liquid of the invention may advantageously be selected from mineral oils, vegetable oils, esters and ethers. It is selected on the basis of conventional criteriae such as viscosity, stability, compatibility with the drilling mud, environmental considerations and
15 availability.

The polysaccharide serving to achieve the desired hardness of the emulsion may for instance be selected from any of the polysaccharides previously utilized for well control. The
20 currently most preferred polysaccharides are xanthanes, alginates and scleroglucanes due to their combination of good crosslinking properties and viscosity characteristics.

Any of the commonly used crosslinking agents for polysaccharides may be used, especially such crosslinking agents that
25 are stable at pH values in the range of 11 to 13. A preferred class of crosslinking agents is constituted by those containing divalent or trivalent metal ions as the active moiety. Examples of such crosslinking agents are Ca(OH)_2 , CaSO_4 and
30 $\text{Al}_2(\text{SO}_4)_3$. Another class of preferred crosslinking agents is constituted by aldehydes, such as glutaric aldehyde.

In addition to the above-mentioned main constituents the plugging liquid of the invention may contain a water-absorbing
35 material in the continuous phase, i.e. the "oil" phase. As a water-absorbing material, a clay mineral would be preferred, in particular bentonite. By being incorporated in the "oil" phase, the water-absorbent material will be kept separated from the water contained in the aqueous phase, until the

emulsion is broken by being subjected to high shear forces. The water-absorbent material will then come into contact with the water contained in the aqueous phase of the emulsion and will absorb excess amounts thereof, whereby said water-absorbent material will undergo swelling, as explained above in the discussion of the plugging liquid of US Pat. No. 4,663,366. In the new plugging liquid, however, the primary function of the water-absorbent material is to absorb free water after the breaking of the emulsion and thus to prevent a shrinking of the material in Condition 2.

Preferably the plugging liquid of the invention comprises:

a) 20 - 40% by volume of a continuous phase containing:

- 900 - 997 ml/l of a hydrophobic liquid,
- 1 - 50 ml/l of an emulsifier, and
- 2 - 50 g/l of a crosslinking agent for a polysaccharide,

b) 60 - 80% by volume of a discontinuous phase containing:

- 970 - 995 ml/l of water, and
- 5 - 30 g/l of a polysaccharide.

A particularly preferred plugging liquid of the invention consists of a water-in-oil emulsion constituted by:

a) about 25% by volume of an oil phase containing:

- about 968 ml/l of a low-aromatic lamp oil,
- about 12 ml/l of an emulsifier on a triglyceride basis,
- about 16 g/l of bentonite, and
- about 24 g/l of calcium hydroxide,

b) about 75% by volume of an aqueous phase containing:

- about 992 ml/l of water and
- about 8 g/l of xanthane.

According to a variant of the invention, a plugging liquid of the above-described sort may contain a weighting material in addition to the constituents already mentioned, whereby the plugging liquid may be used for inhibiting or preventing undesired blow-outs in or from a well. The purpose of using a weighting material in the plugging liquid is to increase the

density thereof so as to put the plugging liquid in a better condition to resist the blow-out pressure in the well.

A serious problem that may arise during the drilling of wells or in the production of oil and gas from wells is blow-out. Surface blow-outs occur when the drill bit cuts into a high pressure zone of gas, oil or water which can blow out the drilling mud and in serious cases even the drill stem with drill bit and other equipment and cause serious damage. 10 Underground blow-out occurs when a fluid in one porous formation flows into the well bore and then out of the well bore into another porous formation.

A common method of trying to stop blow-outs involves loading 15 up the well with a slurry of weighting material, e.g. barite, under pressure and under conditions such that the barite is able to settle uniformly at the bottom of the well to form a hard plug, and then following up with a cement slurry in order to make the plug stronger and more permanent.

20 Another method consists in utilizing a slurry of a dry, powdered bentonite in diesel oil. When this slurry is mixed with the right amount of water, the bentonite will hydrate, yielding a stiff paste. If formed at the right time and at the 25 right place, the mass may provide an effective plugging of the well, see for example US Pat. No. 3,082,823.

US Pat. No. 2,890,169 discloses plugging of a well with a plugging liquid prepared by forming first a slurry of an 30 organophilic bentonite and cement in an oil, and then mixing the obtained slurry with a surfactant and water, to obtain a water-in-oil emulsion wherein the organophilic bentonite and the cement are dispersed in the continuous oil phase. As this emulsion is pumped down the well bore, the oil expands and 35 flocculates the bentonite, which, under the right conditions, forms a filter cake on the well bore surface in the area to be plugged. This is then supposed to cause a filtration action which breaks the emulsion, whereby the emulsified water is brought into contact with the cement and reacts with the

cement to form a solid coating on the filter cake, which completes the plugging.

When the above-described new plugging liquid is used, with any necessary minor adaptations, together with a weighting material, it has been found that a better plugging effect can be achieved than with the slurries and emulsions containing weighting material heretofore employed for plugging well bores.

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Thus, the invention also provides a plugging liquid on an emulsion basis for well control, containing a weighting material, which plugging liquid is characterized by being constituted by an emulsion comprising:

- 15 a) 5 - 50% by volume of a continuous phase containing:
800 - 998.5 ml/l of a hydrophobic liquid,
0.5 - 100 ml/l of an emulsifier, and
1 - 100 g/l of a crosslinking agent for a polysaccharide,
- 20 b) 50 - 95% by volume of a discontinuous phase containing:
600 - 983 ml/l of water,
3 - 50 g/l of a polysaccharide, and
100 - 2500 g/l of a weighting material.

25 This variant of the new plugging liquid will be particularly useful in connection with underground blow-outs in those cases where it will be possible to pump the plugging liquid down the drill stem and through the drill bit. When the emulsion passes through the drill bit and consequently is subjected to high
30 shear forces, a crosslinking of the polysaccharide is initiated by means of the crosslinking agent and the setting of the emulsion will make a substantial contribution to the well-killing effect achieved as a result of the high density of the emulsion.

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Any weighting material can be used in the weighted plugging liquid of the invention. Exemplary weighting materials are barite, ilmenite, hematite, steel balls and calcium carbonate. A particularly suitable weighting material is barite.

The other constituents of the weighted plugging liquid of the invention, i.e. the hydrophobic liquid, the polysaccharide, the crosslinking agent for the polysaccharide, and the emulsifier, can be selected as for the non-weighted plugging liquid of the invention, as described above for said non-weighted plugging liquid.

When the plugging liquid of the invention is to be used for permanent closing of a well, the plugging liquid may also, if desired, contain an additive to prevent circulation loss, such as crushed nut shells or mica folium.

The weighted plugging liquid of the invention is preferably constituted by an emulsion comprising:

- 15 a) 5 - 50% by volume of a continuous phase containing:
800 - 998.5 ml/l of a hydrophobic liquid,
0.5 - 100 ml/l of an emulsifier, and
1 - 100 g/l of a crosslinking agent for a polysaccharide,
- 20 b) 50 - 95% by volume of a discontinuous phase containing:
600 - 983 ml/l of water,
3 - 50 g/l of a polysaccharide, and
100 - 2500 g/l of a weighting material.

25 More preferably, the weighted plugging liquid of the invention is constituted by an emulsion comprising:

- a) 20 - 40% by volume of a continuous phase containing:
900 - 997 ml/l of a hydrophobic liquid,
1 - 50 ml/l of an emulsifier, and
30 2 - 50 g/l of a crosslinking agent for a polysaccharide,
- b) 60 - 80% by volume of a discontinuous phase containing:
620 - 850 ml/l of water,
5 - 30 g/l of a polysaccharide, and
35 100 - 2500 g/l of a weighting material.

A particularly preferred weighted plugging liquid of the invention is constituted by a water-in-oil emulsion consisting of:

- a) about 25% by volume of an oil phase containing:
about 968 ml/l of a low-aromatic lamp oil,
about 12 ml/l of an emulsifier on a triglyceride basis,
about 16 g/l of bentonite, and
about 24 g/l of calcium hydroxide,
- b) about 75% by volume of an aqueous phase containing:
about 682 ml/l of water,
about 8 g/l of xanthane, and
about 1300 g/l of barite.

The invention also provides a method for preparing the new plugging liquid, which method is characterized by mixing the hydrophobic liquid, the emulsifier, the crosslinking agent and any optional water-absorbent material to a mixture (a), mixing the water and the polysaccharide to a mixture (b), and introducing mixture (b) gradually into mixture (a) under agitation to form an emulsion of water in the hydrophobic liquid. When the plugging liquid shall contain a weighting material, said weighting material is incorporated into mixture (b) together with the water and the polysaccharide.

For the purpose of obtaining a stable emulsion it is common practice to include a suitable emulsifier in the continuous phase. The emulsifier can be selected from a broad range of commercially available emulsifiers. The emulsifier should preferably have an alkali resistance such that it is stable in the pH range of 11 to 13 at typical drill hole temperatures. Emulsifiers on a triglyceride basis are very suitable for use in the plugging liquid of the invention. Based on conventional criteriae which will be well known to those skilled in the art, such combinations of hydrophobic liquid and emulsifier are selected which will provide pH stability and the desired emulsion strength for handling and storing the emulsion, but which result in a breaking of the emulsion when the emulsion is pumped through the nozzles of a drill bit down in a drill hole.

The invention further provides a method for plugging a zone of

a subterranean formation penetrated by a drill hole in fluid communication with said zone, in which method an aqueous plugging liquid containing a polysaccharide is injected into the zone via the drill hole, and is subjected to high shear forces in the drill hole, e.g. by passing through the nozzles of a drill bit. The method is characterized by there being used as plugging liquid an emulsion comprising:

a) 5 - 50% by volume of a continuous phase containing:

800 - 998.5 ml/l of a hydrophobic liquid,
0.5 - 100 ml/l of an emulsifier, and
1 - 100 g/l of a crosslinking agent for a polysaccharide,

b) 50 - 95% by volume of a discontinuous phase containing:

950 - 997 ml/l of water, and
3 - 50 g/l of a polysaccharide,

whereby, as a result of the emulsion being subjected to said high shear forces, the polysaccharide and the crosslinking agent are brought into contact with one another, with a resulting initiation of crosslinking of the polysaccharide and setting of the plugging liquid.

The weighted variant of the plugging liquid of the invention is used primarily to inhibit or prevent undesired blow-outs in or from a well bore.

In Condition 1 the plugging liquid should be maintained under gentle agitation and at ambient temperature below 40°C. In preferred embodiments the plugging liquid contains no environmentally harmful or noxious constituents.

The plugging liquid of the invention is not affected by being pumped with a centrifugal pump or mud pump for several hours. However, when the emulsion is subjected to high shear forces, such as when it is forced through the nozzles of a drill bit at a pressure drop of 50 to 120 bars, e.g. about 100 bars, the emulsion sets markedly. The setting time for a non-weighted plugging liquid of the invention can be adjusted e.g. in the range of from 2 to 10 minutes, whereas the setting time for a weighted plugging liquid of the invention can be more appro-

priately adjusted to be within the range of from 2 seconds to 2 minutes, e.g. from 5 to 20 seconds.

The setting time can be predetermined through an appropriate selection of the amounts of crosslinking agent and emulsifier, especially the amount of emulsifier. An increased amount of emulsifier increases the setting time, whereas an increased amount of crosslinking agent reduces the setting time.

- 10 The preparation of the new plugging liquid and its characteristics are shown in more detail in the following examples.

Example 1. Non-weighted plugging liquid.

One liter of a water-in-oil emulsion was prepared in the following manner. 0.75 l. of water and 4.0 g of xanthane were mixed under agitation in a 2 l cup (Cup 1), and likewise 0.25 l "Exxsol D60", 3 ml "Emulsogen" (non-ionic fatty acid ester) and 5.0 g Ca(OH)_2 were mixed in another 2 l cup (Cup 2) under agitation. The mixture in Cup 1 was then added to the mixture in Cup 2 under agitation.

The obtained emulsion was pumped at a pressure of 60 bars through a nozzle and down into a cup where it set in the course of 5 minutes. After 24 hours the shearing stress was measured to be 6000 Pa.

During the setting of the emulsion, a certain amount of free water separated. This may be avoided by incorporating a water-absorbent material, such as bentonite, in the oil based mixture (Cup 2). This was made in Example 2.

Example 2. Non-weighted plugging liquid.

150 l of a water-in-oil emulsion were prepared, consisting of:

- a) 25% by volume of an oil phase containing:

968 ml/l oil of "Exxsol D60",
12 ml/l of "Emulsogen",
16 g/l of bentonite,
24 g/l of calcium hydroxide,

- b) about 75% by volume of an aqueous phase containing:

992 ml/l of water and
8 g/l of xanthane.

112 l of water and 900 g of xanthane in powdery form were
5 mixed in a 2200 l vessel (Vessel 1) equipped with a propeller
mixer operated at 400 r.p.m.. 37 l of "Exxsol D60" (a low-
aromatic lamp oil), 300 ml "Emulsogen" (non-ionic fatty acid
ester), 900 g of milled $\text{Ca}(\text{OH})_2$ and 600 g of bentonite i powder
10 form were mixed in a 1200 l vessel (Vessel 2) equipped with a
propeller mixer operated at 400 r.p.m. The xanthane mixture in
Vessel 1 was then gradually transferred at about 20°C to
Vessel 2 in 8 minutes under agitation at 400 r.p.m.

The obtained emulsion had a density of about 0.95 g/ml. It was
15 not affected by being pumped with a centrifugal pump for 2
hours, during which period the temperature increased from 20
to 40°C. The test was repeated after 24 hours with the same
result.

20 Circular pumping with a centrifugal pump, leading to an
increase of the temperature to 62°C, resulted in the emulsion
setting in the mixing vessel in Condition 1. However, the
shear stress was not measurable, and thus was lower than 200
Pa. This suggests that the stability is reduced when the
25 temperature of the emulsion increases from 40°C to 60°C in the
emulsion. However, since the set emulsion still remained in
Condition 1, it could again be agitated to form a liquid,
homogenous state.

30 After having been subjected to a pressure drop of 100 bars
through a needle valve the emulsion set markedly after 2
minutes. The following shearing stress values were measured at
room temperature:

	After 10 minutes:	8000 Pa
35	After 24 hours:	10-12.000 Pa
	After 2 days (48 hours):	10-12.000 Pa.

No free water or oil was observed.

Example 3. Weighted plugging liquid.

1.362 liters of a water-in-oil emulsion were prepared in the following manner. 0.75 l of water and 6.0 g of xanthane were mixed under agitation in a 2 l cup (Cup 1). The mixture
5 was allowed to rest for 1 hour, whereupon 1800 g of ilmenite were added to the mixture. In another 2 l cup (Cup 2) 0.25 liter of "Exxsol D60", 1.0 ml "Safemul PE" (an emulsifier on a triglyceride basis) and 8.0 g of Ca(OH)_2 were mixed under agitation. The mixture in Cup 1 was then added to the mixture
10 in Cup 2 under agitation. An emulsion having a density of 2.0 g/cm^3 was obtained.

The obtained emulsion was pumped at a pressure of 60 bars through a nozzle and into a cup where it set in the course of
15 1 minute. After 24 hours the shearing stress was measured to be 16000 Pa.

During the setting of the emulsion, a certain amount of free water separated. This may be avoided by incorporating a water-
20 absorbent material, such as bentonite, in the oil based mixture (Cup 2).

Example 4. Weighted plugging liquid.

1.375 liters of a water-in-oil emulsion were prepared in the
25 following manner. 0.75 l of water and 6.0 g of xanthane were mixed under agitation in a 2 l cup (Cup 1). The mixture was allowed to stand for 1 hour, whereupon 1500 g of barite were added to the mixture. In another 2 l cup (Cup 2) 0.25 liter of "Exxsol D60", 1.0 ml "Safemul PE" (an emulsifier on a trigly-
30 ceride basis) and 8.0 g of Ca(OH)_2 were mixed under agitation. The mixture in Cup 1 was then added to the mixture in Cup 2 under agitation. An emulsion having a density of 1.80 g/cm^3 was obtained.

35 The obtained emulsion was pumped at a pressure of 60 bars through a nozzle and into a cup where it set in the course of 2 minutes. After 24 hours the shearing stress was measured to be 14000 Pa.

During the setting of the emulsion, a certain amount of free water separated out. This may be avoided by incorporating a water-absorbent material, such as bentonite, in the oil based mixture (Cup 2).

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Patent claims

1. A plugging liquid for plugging a zone of a subterranean
5 formation around a drill hole, consisting of an aqueous liquid
containing a polysaccharide,
c h a r a c t e r i z e d in that it is constituted by an
emulsion comprising:
- a) 5 - 50% by volume of a continuous phase containing:
- 10 800 - 998.5 ml/l of a hydrophobic liquid,
 0.5 - 100. ml/l of an emulsifier, and
 1 - 100 g/l of a crosslinking agent for a
 polysaccharide,
- b) 50 - 95% by volume of a discontinuous phase containing:
- 15 950 - 997 ml/l of water, and
 3 - 50 g/l of a polysaccharide.
2. The plugging liquid according to claim 1,
c h a r a c t e r i z e d in that it comprises:
- 20 a) 20 - 40% by volume of a continuous phase containing:
- 900 - 997 ml/l of a hydrophobic liquid,
 1 - 50 ml/l of an emulsifier, and
 2 - 50 g/l of a crosslinking agent for a
 polysaccharide,
- 25 b) 60 - 80% by volume of a discontinuous phase containing:
- 970 - 995 ml/l of water, and
 5 - 30 g/l of a polysaccharide.
3. The plugging liquid according to claim 1 or 2,
30 c h a r a c t e r i z e d in that the hydrophobic liquid is
selected from mineral oils, vegetable oils, esters and ethers.
4. The plugging liquid according to any of claims 1 to 3,
c h a r a c t e r i z e d in that the crosslinking agent for
35 crosslinking the polysaccharide contains divalent or trivalent
metal ions as the active moiety.
5. The plugging liquid according to any of claims 1 to 3,
c h a r a c t e r i z e d in that the crosslinking agent is

an aldehyde.

6. The plugging liquid according to any of claims 1 to 5,
c h a r a c t e r i z e d in that the polysaccharide is a
5 xanthane, an alginate or a scleroglucane.

7. The plugging liquid according to any of claims 1 to 6,
c h a r a c t e r i z e d in that the hydrophobic liquid
contains a water-absorbing material.

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8. The plugging liquid according to claim 7,
c h a r a c t e r i z e d in that the water-absorbing
material is a clay mineral, especially bentonite.

15 9. The plugging liquid according to any of claims 1 to 8,
c h a r a c t e r i z e d in that the emulsifier has an
alkali resistance such that it is stable at pH 11 to 13.

10. The plugging liquid according to claim 9,
20 c h a r a c t e r i z e d in that the emulsifier is on a
triglyceride basis.

11. The plugging liquid according to any of claims 1 to 10,
c h a r a c t e r i z e d in that it is a water-in-oil
25 emulsion consisting of:

- a) about 25% by volume of an oil phase containing:
 - about 968 ml/l of a low-aromatic lamp oil,
 - about 12 ml/l of an emulsifier on triglyceride
basis,
 - 30 about 16 g/l of bentonite, and
 - about 24 g/l of calcium hydroxide,
- b) about 75% by volume of an aqueous phase containing:
 - about 992 ml/l of water and
 - about 8 g/l of xanthane.

35

12. A method for plugging a zone of a subterranean formation
penetrated by a drill hole in fluid communication with said
zon , in which an aqueous plugging liquid containing a
polysaccharide is injected into said zone via the drill hole,

and is subjected to high shear forces in the drill hole, e.g. by passing through the nozzles of a drill bit, characterized by there being used as plugging liquid an emulsion comprising:

- 5 a) 5 - 50% by volume of a continuous phase containing:
- | | |
|-------------|---|
| 800 - 998.5 | ml/l of a hydrophobic liquid, |
| 0.5 - 100 | ml/l of an emulsifier, and |
| 1 - 100 | g/l of a crosslinking agent for a polysaccharide, |
- 10 b) 50 - 95% by volume of a discontinuous phase containing:
- | | |
|------------|--------------------------|
| 950 - 997. | ml/l of water, and |
| 3 - 50 | g/l of a polysaccharide, |

whereby, as a result of the emulsion being subjected to said high shear forces, the polysaccharide and the crosslinking agent are brought into contact with one another, with a resulting initiation of crosslinking of the polysaccharide and setting of the plugging liquid.

13. The method according to claim 12, characterized by there being used a plugging liquid according to any of claims 2 to 11.

14. A plugging liquid on an emulsion basis for well control, containing a weighting material, characterized in that it is constituted by an emulsion comprising:

- 25 a) 5 - 50% by volume of a continuous phase containing:
- | | |
|-------------|---|
| 800 - 998.5 | ml/l of a hydrophobic liquid, |
| 0.5 - 100 | ml/l of an emulsifier, and |
| 30 1 - 100 | g/l of a crosslinking agent for a polysaccharide, |
- b) 50 - 95% by volume of a discontinuous phase containing:
- | | |
|---------------|------------------------------|
| 600 - 983 | ml/l of water, |
| 3 - 50 | g/l of a polysaccharide, and |
| 35 100 - 2500 | g/l of a weighting material. |

15. The plugging liquid according to claim 14, characterized in that it comprises:

- a) 20 - 40% by volume of a continuous phase containing:

900 - 997 ml/l of a hydrophobic liquid,
1 - 50 ml/l of an emulsifier, and
2 - 50 g/l of a crosslinking agent for a
polysaccharide,

5 b) 60 - 80% by volume of a discontinuous phase containing:

650 - 850 ml/l of water,
5 - 30 g/l of a polysaccharide, and
1000 - 2500 g/l of a weighting material.

10 16. The plugging liquid according to claim 14 or 15,
c h a r a c t e r i z e d in that the hydrophobic liquid is
selected from mineral oils, vegetable oils, esters and ethers.

17. The plugging liquid according to any of claims 14 to 16,
15 c h a r a c t e r i z e d in that the crosslinking agent for
crosslinking the polysaccharide contains divalent or trivalent
metal ions as the active moiety.

18. The plugging liquid according to any of claims 14 to 17,
20 c h a r a c t e r i z e d in that the crosslinking agent is
an aldehyde.

19. The plugging liquid according to any of claims 14 to 18,
c h a r a c t e r i z e d in that the polysaccharide is a
25 xanthane, an alginate or a scleroglucane.

20. The plugging liquid according to any of claims 14 to 19,
c h a r a c t e r i z e d in that the emulsifier is on a
triglyceride basis.

30 21. The plugging liquid according to any of claims 14 to 20,
c h a r a c t e r i z e d in that hydrophobic liquid
contains a water-absorbing material.

35 22. The plugging liquid according to claim 21,
c h a r a c t e r i z e d in that the water-absorbing
material is a clay mineral, especially bentonite.

23. The plugging liquid according to any of claims 14 to 22,

c h a r a c t e r i z e d in that the weighting material is selected from barite, ilmenite, hematite, steel balls and potassium carbonate.

5 24. The plugging liquid according to claim 23,
c h a r a c t e r i z e d in that the weighting material is barite.

25. The plugging liquid according to any of claims 19 to 24,
10 c h a r a c t e r i z e d in that it is a water-in-oil emulsion consisting of:

a) about 25% by volume of an oil phase containing:
about 968 ml/l of a low-aromatic lamp oil,
about 12 ml/l of an emulsifier on a triglyceride
15 basis,
about 16 g/l of bentonite, and
about 24 g/l of calcium hydroxide,

b) about 75% by volume of an aqueous phase containing:
about 682 ml/l of water,
20 about 8 g/l of xanthane, and
about 1300 g/l of barite.

26. The plugging liquid according to any of claims 14 to 25,
c h a r a c t e r i z e d in that the emulsifier has an
25 alkali resistance such that it is stable at pH 11 to 13.

27. A method for preparing a plugging liquid according to any
of claims 14 to 26,
c h a r a c t e r i z e d b y mixing the hydrophobic liquid,
30 the emulsifier, the crosslinking agent and optional water-
absorbent material to form a mixture (a), mixing the water,
the polysaccharide and the weighting material to form a
mixture (b), and introducing mixture (b) gradually into
mixture (a) under agitation to form an emulsion of water in
35 the hydrophobic liquid.

28. A use of a plugging liquid according to any of claims 14
to 26 for inhibiting or preventing an undesired blow-out in or
from a well.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 94/00097

A. CLASSIFICATION OF SUBJECT MATTER

IPC : C09K 7/02, C09K 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EDOC, WPI, USPM, CLAIMS, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3979303 (K S KANG ET AL.), 7 Sept 1976 (07.09.76), claims 1,3,4,8 --	1,12,14,27, 28
A	EP, A2, 0226250 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 24 June 1987 (24.06.87), page 2, line 47 - line 49, claims 1,10 --	1,12,14,27, 28
A	EP, A2, 0137538 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ), 17 April 1985 (17.04.85), page 1, line 1 - page 2, line 29 --	1,12,14,27, 28
A	EP, A1, 0128661 (ALLIED COLLOIDS LIMITED), 19 December 1984 (19.12.84), claims 1,18,19 --	1,12,14,27, 28

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 August 1994

Date of mailing of the international search report

02 -09- 1994

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 94/00097

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Derwent's abstract, No 89-307380/42, week 8942, ABSTRACT OF SU, 1447832 (UKHTINSK), 30 December 1988 (30.12.88) -----	1, 12, 14, 27, 28

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 94/00097

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-7, 9, 11, 17-21, 23, 25-26
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/07/94

International application No.

PCT/NO 94/00097

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3979303	07/09/76	NONE	
EP-A2- 0226250	24/06/87	DE-A- 3681133	02/10/91
		JP-A- 62153328	08/07/87
		US-A- 4803264	07/02/89
EP-A2- 0137538	17/04/85	SE-T3- 0137538	
		AU-A- 2971489	24/08/89
		AU-A- 3276184	14/03/85
		CA-A- 1232820	16/02/88
		JP-B- 6015634	02/03/94
		JP-A- 60072938	25/04/85
		US-A- 4670167	02/06/87
		CA-A- 1231616	19/01/88
		US-A- 4670550	02/06/87
EP-A1- 0128661	19/12/84	AU-B- 581616	02/03/89
		AU-A- 2806784	22/11/84
		CA-A- 1239014	12/07/88
		JP-A- 59233092	27/12/84
		US-A- 4571422	18/02/86
		US-A- 4950747	21/08/90
		US-A- 4950748	21/08/90

Form PCT/ISA/210 (patent family annex) (July 1992)